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ATTORNEY'S DOCKET NUMBER  
107291

**TRANSMITTAL LETTER TO THE  
UNITED STATES  
DESIGNATED/ELECTED OFFICE  
(DO/EO/US) CONCERNING A FILING  
UNDER 35 U.S.C. 371**

U.S. APPLICATION NO.  
(if known, sec 37 C.F.R.1.5)

09/701534

INTERNATIONAL APPLICATION NO.  
PCT/JP00/01987INTERNATIONAL FILING DATE  
March 29, 2000PRIORITY DATE CLAIMED  
March 30, 1999TITLE OF INVENTION  
METHOD FOR FORMING SILICON FILM AND INK COMPOSITION FOR INK JET

## APPLICANTS FOR DO/EO/US

Shunichi SEKI, Tatsuya SHIMODA, Satoru MIYASHITA, Masahiro FURUSAWA, Ichio YUDASAKA, Yasuo MATSUKI, Yasumasa TAKEUCHI

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☐ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☒ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventors (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

**Items 11. to 16. below concern other document(s) or information included:**

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.  
☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ Entitlement to small entity status is hereby asserted.
16. ☒ Other items or information: PCT Request, Request for Approval of Drawing Corrections

OFFICE OF THE ATTORNEY GENERAL

U.S. APPLICATION NO. (if known, see 37 C.F.R. 1.5) <b>09/701534</b>		INTERNATIONAL APPLICATION NO. PCT/JP00/01987		ATTORNEY'S DOCKET NUMBER 107291	
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17. <input checked="" type="checkbox"/> The following fees are submitted:  <b>Basic National fee (37 CFR 1.492(a)(1)-(5)):</b>  Search Report has been prepared by the EPO or JPO .... \$860.00  International preliminary examination fee paid to USPTO (37 CFR 1.482) ..... \$690.00  No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) ..... \$710.00  Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$1,000.00  International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) ..... \$ 100.00  <b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b> \$860.00				CALCULATIONS		PTO USE ONLY	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$			
Claims	Number Filed	Number Extra	Rate				
Total Claims	22- 20 =	2	X \$ 18.00	\$36.00			
Independent Claims	4- 3 =	1	X \$ 80.00	\$80.00			
Multiple dependent claim(s)(if applicable)			+ \$270.00	\$			
<b>TOTAL OF ABOVE CALCULATIONS =</b>				\$976.00			
Reduction by 1/2 for filing by small entity, if applicable.				-			
<b>SUBTOTAL =</b>				\$976.00			
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 month from the earliest claimed priority date (37 CFR 1.492(f)).				\$			
<b>TOTAL NATIONAL FEE =</b>				\$976.00			
				Amount to be refunded	\$		
				Charged	\$		


a. ☒ Check No. 114231 in the amount of \$976.00 to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \$\_\_\_\_\_ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Director is hereby authorized to charge any additional fees which may be required, or credit any overpayment, to Deposit Account No. 15-0461. A duplicate copy of this sheet is enclosed.

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.**

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 REGISTRATION NUMBER: 27,075  
  
 NAME: Christian Austin-Hollands  
 REGISTRATION NUMBER: 46,527

526 Rec'd PC7/F70 30 NOV 2000

## PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of

Shunichi SEKI, Tatsuya SHIMODA,  
Satoru MIYASHITA, Masahiro FURUSAWA,  
Ichio YUDASAKA, Yasuo MATSUKI,  
Yasumasa TAKEUCHI

Application No.: U.S. National Stage of  
PCT/JP00/01987

Filed: November 30, 2000

Docket No.: 107291

For: METHOD FOR FORMING SILICON FILM AND INK COMPOSITION FOR INK JET

PRELIMINARY AMENDMENT

Director of the U.S. Patent and Trademark Office  
Washington, D. C. 20231

Sir:

Prior to initial examination, please amend the above-identified application as follows:

IN THE ABSTRACT:

Please substitute the attached Abstract for the Abstract currently in the application.

IN THE SPECIFICATION:

Please amend the specification as follows:

Page 1, line 1, delete "DESCRIPTION"; and

line 5, change "TECHNICAL FIELD" to --BACKGROUND OF THE

INVENTION--;

between lines 5 and 6, insert --1. Field of the Invention--:

line 11, change "BACKGROUND ART" to --2. Description of the Related Art--.

Page 3, line 15, change "DISCLOSURE OF INVENTION" to --SUMMARY OF THE INVENTION--.

Page 5, line 17, change "BEST MODE FOR CARRYING OUT THE INVENTION" to --DETAILED DESCRIPTION OF THE EMBODIMENTS--.

Page 10, line 30, delete "1,2-dimethyloxyene, bis(2-methyloxyethyl)ether,".

Page 11, line 19, delete "These solvents may contain a surface tension modifier, such as a fluorine type, a silicon type, or a nonionic type, in a trace amount, if necessary, within a range which does not impair required functions.".

Page 18, line 29, change "25n" to --65n--.

Page 19, line 1, change "25p" to --65p--;

line 9, change "26n and 26p" to --66n and 66p--.

IN THE CLAIMS:

Please amend claims 1-22 as follows:

1. (Amended) A method for forming a silicon film, comprising:  
applying by patterning an ink composition containing a silicon compound onto a substrate by an ink jet process.
2. (Amended) [A] The method for forming a silicon film according to claim 1, [wherein] the ink composition [is] being applied in an inert atmosphere.
3. (Amended) [A] The method for forming a silicon film according to [either] claim 1 [or 2], further comprising[, after applying the ink composition containing the silicon compound onto the substrate by the ink jet process,]; a drying step of removing a solvent of the composition; and

a step of pyrolyzing [an/or] and/or photolyzing in the coating film.

4. (Amended) [A] The method for forming a silicon film according to claim 3, further comprising:

a step for irradiating the silicon film formed by the heat treatment and/or the light treatment with laser to convert the amorphous silicon film into a polycrystalline silicon film.

5. (Amended) [A] The method for forming a silicon film according to claim 1, [wherein] the silicon compound is a silicon compound represented by [the following general formula (I):]



[wherein] n [represents] representing an integer 3 or more, m [represents] representing an integer of n, 2n-2, 2n, or 2n+2, and X [represents] representing a hydrogen atom and/or a halogen atom.

6. (Amended) [A] The method for forming a silicon film according to claim 1, [wherein] the silicon compound is a silicon compound represented by [the following general formula (II):]



[wherein] X [represents] representing a hydrogen atom and/or a halogen atom, Y [represents] representing a boron atom or a phosphorus atom, a [represents] representing an integer of 3 or more, b [represents] representing an integer of a to 2a+c+2, and c [represents] representing an integer of 1 to a.

7. (Amended) [A] The method for forming a silicon film according to claim 1, [wherein] the silicon compound is a composition containing a silicon compound represented by the following general formula [(I)] and a silicon compound represented by [the following general formula (II):]



[wherein] n [represents] representing an integer 3 or more, m [represents] representing an integer of n, 2n-2, 2n, or 2n+2, and X [represents] representing a hydrogen atom and/or a halogen atom; and

silicon compound represented by



[wherein] X [represents] representing a hydrogen atom and/or a halogen atom, Y [represents] representing a boron atom or a phosphorus atom, a [represents] representing an integer of 3 or more, b [represents] representing an integer of a to 2a+c+2, and c [represents] representing an integer of 1 to a.

8. (Amended) [A] The method for forming a silicon film according to [either] claim 5 [or 7], [wherein] n [is] being in a range of 5 to 20 [in the general formula (I)].

9. (Amended) [A] The method for forming a silicon film according to [either] claim 6 [or 7], [wherein] a+c [is] being in a range of 5 to 20 [in the general formula (II)].

10. (Amended) [A] The method for forming a silicon film according to [any one of claims 1 to 9] claim 1, [wherein, in the composition], the silicon compound [is] being dissolved in at least one solvent having a vapor pressure at room temperature of 0.001 to 50 mmHg.

11. (Amended) [A] The method for forming a silicon film according to claim 10, [wherein] the solvent [is] being a hydrocarbon solvent.

12. (Amended) [A] The method for forming a silicon film according to [any one of claims 1 to 11] claim 1, [wherein] the concentration of the silicon compound in the composition [is] being in a range of 0.01 to 10 percent by weight.

13. (Amended) [A] The method for forming a silicon film according [to any one of claims 1 to 12] claim 1, [wherein] the concentration [has] being a viscosity of 1 to 50 mPa·s and a surface tension of 20 to 70 dyn/cm.

14. (Amended) An ink-jet ink composition for forming a silicon film, comprising:  
a silicon compound represented [by the general formula (I):]



[wherein] n [represents] representing an integer 3 or more, m [represents] representing an integer of n, 2n-2, 2n, or 2n+2, and X [represents] representing a hydrogen atom and/or a halogen atom.

15. (Amended) An ink-jet ink composition for forming a silicon film, comprising:  
a silicon compound represented by [the general formula (II):]



[wherein] X [represents] representing a hydrogen atom and/or a halogen atom, Y [represents] representing a boron atom or a phosphorus atom, a [represents] representing an integer of 3 or more, b [represents] representing an integer of a to 2a+c+2, and c [represents] representing an integer of 1 to a.

16. (Amended) An ink-jet ink composition for forming a silicon film, comprising:  
a silicon compound represented by [the following general formula (I) and a silicon compound represented by the following general formula (II):]



[wherein] n [represents] representing an integer 3 or more, m [represents] representing an integer of n, 2n-2, 2n, or 2n+2, and X [represents] representing a hydrogen atom and/or a halogen atom; and

a silicon compound represented by



[wherein] X [represents] representing a hydrogen atom and/or a halogen atom, Y [represents] representing a boron atom or a phosphorus atom, a [represents] representing an integer of 3 or more, b [represents] representing an integer of a to  $2a+c+2$ , and c [represents] representing an integer of 1 to a.

17. (Amended) [An] The ink composition according to [either] claim 14 [or 16], [wherein] n [is] being in a range of 5 to 20 [in the general formula (I)].

18. (Amended) [An] The ink composition according to [either] claim 15[ or 16], wherein a+c [is] being in a range of 5 to 20 [in the general formula (II)].

19. (Amended) [An] The ink composition according to [any one of claims 14 to 18] claim 14, [wherein] the silicon compound [is] being dissolved in at least one solvent having a vapor pressure at room temperature of 0.001 to 50 mmHg.

20. (Amended) [An] The ink composition according to claim 19, [wherein] the solvent [is] being a hydrocarbon solvent.

21. (Amended) [An] The ink composition according to [any one of claims 14 to 20] claim 14, [wherein] the concentration of the silicon compound in the composition [is] being in a range of 0.01 to 10 percent by weight.

22. (Amended) [An] The ink composition according to [any one of claims 14 to 21] claim 14, [wherein] the concentration [has] having a viscosity of 1 to 50 mPa·s and a surface tension of 20 to 70 dyn/cm.



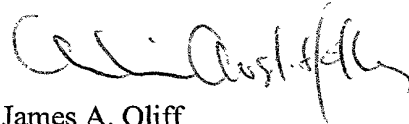
REMARKS

Claims 1-22 are pending. By this Amendment, the specification and claims 1-22 are amended. The specification and claims 1-22 are amended for clarity. No new matter is added.

The above amendments place the application in even better condition for initial examination. Prompt consideration and allowance in due course are earnestly solicited.

Should the Examiner believe anything further is desirable to place the application in even better condition for allowance, the Examiner is invited to contact Applicant's undersigned representative at the telephone number listed below.

Respectfully submitted,



James A. Oliff  
Registration No. 27,075

Christian Austin-Hollands  
Registration No. 46,527

JAO:CAH/cmm

Attachment:  
Substitute Abstract

Date: November 30, 2000

**OLIFF & BERRIDGE, PLC**  
**P.O. Box 19928**  
**Alexandria, Virginia 22320**  
**Telephone: (703) 836-6400**

<p>DEPOSIT ACCOUNT USE AUTHORIZATION Please grant any extension necessary for entry; Charge any fee due to our Deposit Account No. 15-0461</p>
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ABSTRACT

A method for forming a silicon film, comprising, applying by patterning an ink composition containing a silicon compound onto a substrate by an ink jet process for stably forming a desired silicon film pattern with low energy consumption at a low cost, and a method for forming a silicon film without a convention vacuum process, photolithography and etching, in the production of a device having a desired silicon film pattern onto a substrate having a large area. It is another object to provide a composition containing a silicon precursor and a method for patterning a silicon film, in the production of a device having a silicon film doped with boron or phosphorus in which a film comprising a modified silicon compound as a silicon precursor is formed using a solution, and the silicon precursor film is converted into a semiconductive silicon and doping is simultaneously achieved by heat and/or light treatment in an inert atmosphere.

## DESCRIPTION

METHOD FOR FORMING SILICON FILM AND INK COMPOSITION FOR INK  
JET5     TECHNICAL FIELD

The present invention relates to an ink composition containing a silicon precursor for forming, by patterning, a silicon film by an ink jet process in use of LSIs, thin film transistors, and photosensitive devices, and to a method for forming a silicon film by an ink jet process.

10

BACKGROUND ART

As conventional methods for forming amorphous silicon films and polysilicon films, thermal CVD (chemical vapor deposition) processes, plasma enhanced CVD processes, and photo-assisted CVD processes using monosilane gas and disilane gas have been used. In general, thermal CVD processes are widely used for polysilicon films (refer to J. Vac. Sci. Technology, Vol. 14, 1082 (1977)), and plasma enhanced CVD processes are widely used for amorphous silicon films (refer to Solid State Com., Vol. 17, 1193 (1975)). These are used in production of liquid crystal devices having thin film transistors and solar batteries.

20         In the formation of silicon films by these CVD processes, however, further improvements are needed with regard to the following problems: (1) The production yield is low due to system contamination and the formation of foreign materials, which are caused by silicon particles generated during the gas phase reaction; (2) A uniform film thickness is barely obtainable on a substrate having an uneven surface  
25         due to gaseous raw materials; (3) The productivity is low due to a low deposition rate of the film; and (4) The plasma enhanced CVD process requires a complicated and expensive radiofrequency generator and vacuum equipment.

In regard to materials used in the CVD process, the use of silicon hydride, which is highly reactive gas, is difficult to handle, and requires hermetic vacuum

In recent years, a method has been proposed for applying liquid silicon hydride without a vacuum system. Japanese Unexamined Patent Application Publication No. 1-29661 discloses a method for forming a silicon-based thin film in which a gaseous material is liquefied and is adsorbed onto a cooled substrate to react with chemically active, atomic hydrogen. This method, however, has the following problems. Since silicon hydride is required as the raw material for the process, and is continuously gasified and cooled, a complicated apparatus is required and the control of the thickness is difficult.

Moreover, Japanese Unexamined Patent Application Publication No. 9-237927 discloses a method for spray-coating a polysilane solution onto a substrate having a large area and for pyrolyzing the coating to form a silicon film, in order to produce solar batteries. In carbon-containing silicon compounds, a large amount of carbon remains as an impurity in pyrolysis or photolysis by ultraviolet irradiation, hence, it is difficult to prepare an amorphous or polycrystalline silicon film having superior electrical characteristics.

On the other hand, the above Japanese Unexamined Patent Application Publication No. 9-237927 discloses a method for applying a polysilane solution

containing an alkyl compound which imparts p-type or n-type conductivity and a method for pyrolyzing a coating film from a polysilane solution in an atmosphere containing a dopant source. In the former method, however, a uniformly doped film may be unobtainable due to differences in solubility between the polysilane and the dopant-containing alkyl compound, and the final film product inevitably contains a large amount of carbon as an impurity due to carbon contained in the material, as described above. In the latter method, it is difficult to control the dopant.

In a conventional method for forming a silicon film pattern, a silicon film is formed on the entire substrate by the above method, and a required pattern is formed by a photolithographic process or an etching process. When the silicon film is patterned over a large area to form many devices, many production steps must be employed and expensive apparatus and various materials are used, requiring a large amount of energy, which results in high production costs.

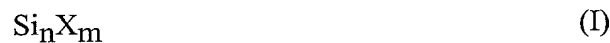
#### DISCLOSURE OF INVENTION

It is an object of the present invention to provide a composition, which is a material for stably forming a desired silicon film pattern with low energy consumption at low cost, and a method for forming a silicon film without a conventional vacuum process, photolithography, and etching, in the production of a device having a desired silicon film pattern onto a substrate having a large area. It is another object to provide a composition containing a silicon precursor and a method for patterning a silicon film, in the production of a device having a silicon film doped with boron or phosphorus in which a film comprising a modified silicon compound as a silicon precursor is formed using a solution, and the silicon precursor film is converted into semiconductive silicon and doping is simultaneously achieved by heat and/or light treatment in an inert atmosphere.

According to the present invention, there is provided a method for forming a silicon film, comprising; applying by patterning an ink composition containing a silicon compound onto a substrate by an ink jet process.

Moreover, the present inventors have intensively researched to achieve the above objects and have discovered that an ink material composition containing a silicon compound represented by the following general formula (I) or (II) exhibits superior material stability, discharge stability, and coating uniformity in an ink jet process, and that the required silicon film pattern can be formed on a substrate by heat and/or light treatment of a silicon precursor coating film from the solution, with satisfactory conversion into the silicon film without incorporation of a solvent.

According to the present invention, there is provided a method for a silicon film pattern, comprising: applying by patterning a composition containing a silicon compound represented by the following general formula (I) or (II) onto a substrate by an ink jet process:



with n representing an integer 3 or more, m representing an integer of n, 2n-2, 2n, or 2n+2, and X representing a hydrogen atom and/or a halogen atom; and



with X representing a hydrogen atom and/or a halogen atom, Y representing a boron atom or a phosphorus atom, a representing an integer of 3 or more, b representing an integer of a to 2a+c+2, and c representing an integer of 1 to a.

It is preferable to use a mixture of the silicon compound represented by the general formula (I) and the silicon compound represented by the general formula (II).

According to the present invention, there is provided a liquid composition containing a silicon compound for ink jet processes comprising a silicon compound represented by the general formula (I) and/or a silicon compound represented by the general formula (II), and a solvent for dissolving the silicon compound, the solvent having a specific viscosity, a specific surface tension, and a specific solid component content.

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a drawing showing patterning steps of a silicon thin film by an ink jet process in accordance with Example 1.

Fig. 2 is a drawing showing patterning steps of a silicon thin film by an ink jet process in accordance with Example 2.

Fig. 3 is a drawing showing patterning steps of a p-type silicon thin film by an ink jet process in accordance with Example 3.

Fig. 4 is a drawing showing patterning steps of an n-type silicon thin film by an ink jet process in accordance with Example 4.

Fig. 5 is a drawing showing patterning steps of a silicon thin film by an ink jet process in accordance with Example 5.

Fig. 6 is a drawing showing patterning steps of a p-type silicon thin film by an ink jet process in accordance with Example 6.

Fig. 7 is a drawing showing patterning steps of a silicon thin film by an ink jet process in accordance with Example 7.

## BEST MODE FOR CARRYING OUT THE INVENTION

The embodiments of the present invention will be described in detail.

The silicon compounds used in the method for forming the silicon film in the present invention are preferably compounds represented by the general formula (I)  $\text{Si}_n\text{X}_m$  with  $n$  representing an integer 3 or more,  $m$  representing an integer of  $n$ ,  $2n-2$ ,  $2n$ , or  $2n+2$ , and  $X$  representing a hydrogen atom and/or a halogen atom, and compounds represented by the general formula (II)  $\text{Si}_a\text{X}_b\text{Y}_c$  with  $X$  representing a hydrogen atom and/or a halogen atom,  $Y$  representing a boron atom or a phosphorus atom,  $a$  representing an integer of 3 or more,  $b$  representing an integer of  $a$  to  $2a+c+2$ , and  $c$  representing an integer of 1 to  $a$ .

In these general formulae (I) and (II),  $n$  represents an integer of 3 or more, and  $a+c$  represents an integer of 4 or more. In consideration of thermodynamic stability, solubility, and feasibility of purification, cyclic silicon compounds with  $n$  of

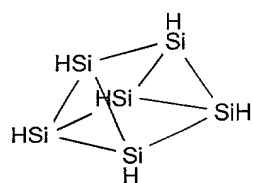
approximately 5 to 20 and particularly 5 or 6 are preferred in the general formula (I), and silicon compounds with a+c of approximately 5 to 20 and particularly 5 or 6 are preferred in the general formula (II). At a value of less than 5, the silicon compound is unstable due to distortion of the ring and handling is difficult. When n and a+c are larger than 20, the solubility decreases due to cohesive force of the silicon compound and selectable solvents are limited.

In the general formulae (I) and (II) for the silicon compounds used in the present invention, X represents a hydrogen atom and/or a halogen atom. Since these silicon compounds are precursors for the silicon films, the silicon compounds must be finally converted into amorphous or polycrystalline silicon by heat and/or light treatment. During the final conversion process, the silicon-hydrogen bonds and the silicon-halogen bonds are cleaved to form silicon-silicon bonds, and converted into silicon. Examples of halogen atoms, include: a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom. Chlorine and bromine are preferable with regard to the bond cleavage. X may be a hydrogen atom alone or a halogen atom alone, or may be a partially halogenated compound, in which the sum of hydrogen atoms and halogen atoms satisfies the general formula (I) or (II).

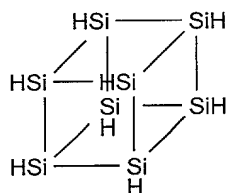
Examples of the silicon compounds represented by the general formula  $\text{Si}_n\text{X}_m$  used in the present invention will be described. Examples of the compounds of  $m = 2n+2$  include silane hydrides, such as: trisilane, tetrasilane, pentasilane, hexasilane, and heptasilane, and substituted compounds thereof in which hydrogen atoms are partially or completely replaced with halogen atoms. Examples of  $m = 2n$  compounds include: monocyclic silicon hydride compounds, such as: cyclotrisilane, cyclotetrasilane, cyclopentasilane, silylcyclopentasilane, cyclohexasilane, silylcyclohexasilane, and cycloheptasilane; and halogenated cyclic silicon compounds thereof in which hydrogen atoms are partially or completely replaced with halogen atoms, such as hexachlorocyclotrisilane, trichlorocyclotrisilane, octachlorocyclotetrasilane, tetrachlorocyclotetrasilane, decachlorocyclopentasilane, pentachlorocyclopentasilane, dodecachlorocyclohexasilane,



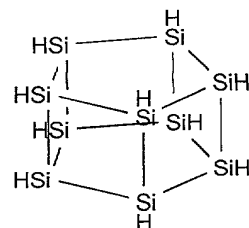
20



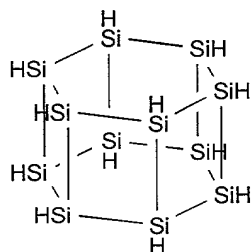
Compound 1



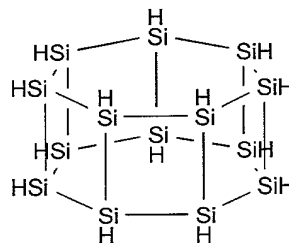
Compound 2



Compound 3



Compound 4

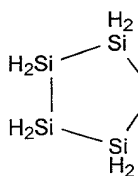


Compound 5

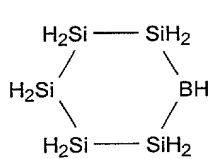
Examples of the compounds represented by the general formula (II)  $\text{Si}_a\text{X}_b\text{Y}_c$

5 used in the present invention include modified silane compounds as shown in

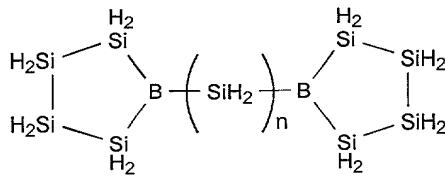
Compounds 6 to 27 represented by the following formulae.



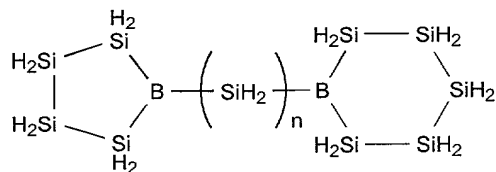
Compound 6



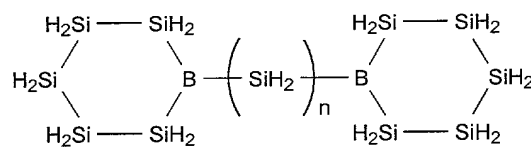
Compound 7



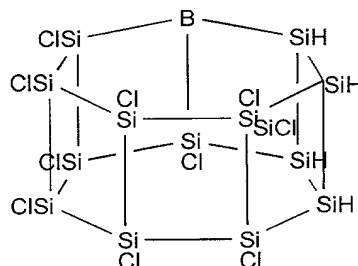
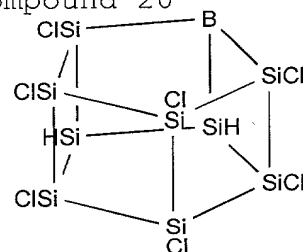
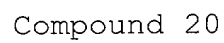
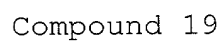
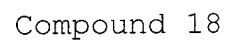
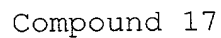
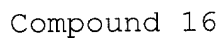
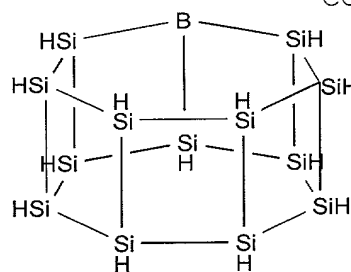
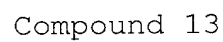
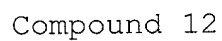
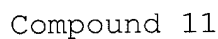
Compound 8



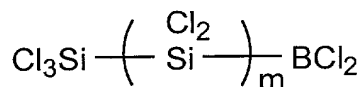
Compound 9



Compound 10



Compound 25



Compound 27

10 In the present invention, the above modified silane compounds may be used alone as a solution, or may be used as a mixture together with the above unmodified silane compounds. The ratio of the modified silane compound to the unmodified silane compound depends on the boron or phosphorus content as a modifying element, and the modifying element is 1 ppb to 25% to silicon atoms.

Solvents used in the present invention, may be, any solvent capable of dissolving the silicon compounds and are unreactive with the silicon compounds.

Examples of the solvents include hydrocarbon solvents, such as: n-heptane, n-octane, decane, toluene, xylene, cymene, durene, indene, dipentene, tetrahydronaphthalene, decahydronaphthalene, and cyclohexylbenzene; ether solvents, such as: ethylene glycol dimethyl ether, ethylene glycol diethyl ether, ethylene glycol methyl ethyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol methyl ethyl ether, 1,2-dimethoxyethane, bis(2-methoxyethyl)ether, and p-

dioxane; and polar solvents, such as propylene carbonate,  $\gamma$ -butyrolactone, N-methyl-2-pyrrolidone, dimethylformamide, dimethyl sulfoxide, and cyclohexanone. Among these, hydrocarbon solvents and ether solvents are preferable in view of solubility of silicon compounds and stability thereof. The hydrocarbon solvents are more preferable. These solvents may be used alone or in combinations of two or more. In particular, the hydrocarbon solvents are advantageous, since these exhibit high solubility of the silicon compounds and suppress the remaining silicon compound after the heat treatment and the light treatment, described below.

In the present invention, the ink composition (solution) applied to the ink jet process is prepared by mixing the above silicon compounds and/or the modified silicon compounds as solutes with the above solvents. The concentration of the solutes are determined depending on the required thickness of the silicon film. Preferably, the concentration is 0.01 to 10 percent by weight. When the concentration is less than 0.01%, a uniform coating film is not obtained and discharge operations must be increased. When the concentration exceeds 10%, the viscosity increases and affects discharge.

These solvents may contain a surface tension modifier, such as a fluorine type, a silicon type, or a nonionic type, in a trace amount, if necessary, within a range which does not impair required functions. These solvents may contain a surface tension modifier, such as a fluorine type, a silicon type, or a nonionic type, in a trace amount, if necessary, within a range which does not impair required functions. The nonionic surface tension modifier improves wettability to a workpiece for applying the solution and leveling of the coating film, and prevents graininess and other surface imperfections, for example, an orange peel surface, of the coating film.

Examples of such nonionic surfactants include fluorinated surfactants having fluoroalkyl groups or perfluoroalkyl groups, and polyether alkyl surfactants having oxyalkyl groups. Examples of fluorinated surfactants include:  $C_9F_{19}CONHC_{12}H_{25}$ ,  $C_8F_{17}SO_2NH-(C_2H_4O)_6H$ ,  $C_9F_{17}O-(PLURONIC\ L-35)-C_9F_{17}$ ,  $C_9F_{17}O-(PLURONIC\ P-84)-C_9F_{17}$ , and  $C_9F_7O-(TETRONIC-704)-(C_9F_{17})_2$ , wherein

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PLURONIC L-35 is a polyoxypropylene-polyoxyethylene block copolymer having an average molecular weight of 1,900 made by Asahi Denka Kogyo K.K., PLURONIC P-84 is a polyoxypropylene-polyoxyethylene block copolymer having an average molecular weight of 4,200 made by Asahi Denka Kogyo K.K., and TETRONIC-704 is an N,N,N',N'-tetrakis(polyoxypropylene-polyoxyethylene) block copolymer having an average molecular weight of 5,000 made by Asahi Denka Kogyo K.K.

Actual examples of the fluorinated surfactants include Efftop EF301, Efftop EF303, and Efftop EF352 made by Shin Akita Kasei K.K.; Megafack F171 and Megafac F173 made by Dainippon Ink and Chemicals; Asahi Guard AG710 made by Asahi Glass Co., Ltd.; Fluorad FC-170C, Fluorad FC430, and Fluorad FC431 made by Sumitomo 3M Limited; Surflon S-382, Surflon SC101, Surflon SC102, Surflon SC103, Surflon SC104, Surflon SC105, and Surflon SC106 made by Asahi Glass Co., Ltd.; BM-1000 and BM-1100 made by B. M-Chemie; and Schsego-Fluor made by Schwegmann.

Polyether alkyl surfactants are polyoxyethylene alkyl ethers, polyoxyethylene allyl ether, polyoxyethylene alkylphenol ethers, polyoxyethylene fatty acid esters, sorbitan fatty acid esters, polyoxyethylene sorbitan fatty acid ethers, and oxyethylene-oxypropylene block copolymers.

Actual examples of these polyether alkyl surfactants include Emulgen 105, Emulgen 430, Emulgen 810, Emulgen 920, Rheodol SP-40S, Rheodol TW-L120, Emanol 3199, Emanol 4110, Excel P-40S, Bridge 30, Bridge 52, Bridge 72, Bridge 92, Arlacel 20, Emasol 320, Tween 20, Tween 60, and Merge 45 made by Kao Corporation; and Nonipol 55 made by Sanyo Chemical Industries, Ltd. Examples of other nonionic surfactants include: polyoxyethylene fatty acid esters, polyoxyethylene sorbitan fatty acid esters, and polyalkylene oxide block copolymers. Actual Examples of these surfactants are Chemistat 2500 made by Sanyo Chemical Industries, Ltd., SN-EX9228 made by San Nopco Limited, and Nonal 530 made by Toho Chemical Industry Co., Ltd.

It is preferable that the viscosity of the prepared silicon-compound-containing solution be within a range of 1 to 50 mPa·s. When the viscosity is lower than 1 mPa·s, the peripheral section of the nozzle in the ink jet process is readily contaminated due to overflow of the ink. When the viscosity is higher than 50 mPa·s, the frequency of nozzle clogging increases to preclude smooth discharge of droplets.

Preferably, the surface tension of the silicon-compound-containing solution is in a range of 20 to 70 dyn/cm. A surface tension of less than 20 dyn/cm causes increased wettability of the ink composition to the nozzle surface, resulting in nonlinear flight. A surface tension exceeding 70 dyn/cm causes an unstable meniscus shape at the nozzle tip, resulting in uncontrollability of the discharged volume and discharging timing of the ink composition.

The droplet discharge apparatus in the ink jet process used for supplying the solution in the present invention may be of any mechanism which can discharge appropriate droplets in constant volumes. The apparatus may be of an ink jet process using a piezoelectric element which can form droplets, each weighting approximately several tens nanograms, or of a bubble jet process which forms bubbles by thermal energy from a heater. Moreover, a general coating process, such as: spin coating, dip coating, spray coating, roll coating, or curtain coating, may be combined, if necessary. When the ink composition containing the silicon precursor is applied by the ink jet process, the atmosphere is generally an inert gas, such as argon, helium, or nitrogen, and the temperature is appropriately selected in a range of room temperature to approximately 100°C depending on the ink characteristics.

In the present invention, the substrate used in discharge of the silicon-compound-containing solution by the ink jet process is not limited. Examples of the substrates include general quartz, borosilicate glass, soda glass, transparent electrodes such as: ITO, metallic substrates, e.g., gold, silver, copper, nickel, titanium, aluminum, and tungsten, and glass or plastic substrates coated with these metals.

The coating film of the silicon-compound-containing solution formed by the ink jet process is subjected to a heat and/or light treatment. The treatment is

performed in an inert gas atmosphere, such as nitrogen, argon, and helium. A small amount of reducing gas such as hydrogen may be added, if necessary. The heat treatment is performed for the removal of the solvent and the conversion into a metallic silicon film, after the coating of the ink (solution). The drying treatment, may be, appropriately determined by the boiling point (vapor pressure) and the pressure of the solvent and thermal behavior of the silicon compound, without particular limitation. The conversion into the metallic silicon film is generally performed in an argon atmosphere at, approximately, 100 to 800°C, preferably approximately, 200 to 600°C, and more preferably 300°C to 500°C. In general, an amorphous silicon film is obtained at a final temperature of 550°C or less, whereas a polycrystalline silicon film is obtained at a higher temperature. At a final temperature of less than 300°C, pyrolysis of the silicon compound does not sufficiently proceed, and a silicon film having a sufficient thickness cannot be formed in some cases. The polycrystalline silicon film may also be prepared by conversion of the above amorphous silicon film into the polycrystalline silicon by laser irradiation. The atmosphere in the laser irradiation is preferably an inert gas, such as helium and argon, and may contain a reducing gas, such as hydrogen.

The coating film of the silicon compound formed by the ink jet process in the present invention, may be, subjected to a light treatment in an inert gas atmosphere before, and/or after, removing the solvent in the coating film. The silicon compound soluble in solvents is converted into a tough coating film, which is insoluble in the solvents, by the ring cleavage reaction, by means of this light treatment. Moreover, the heat treatment, which is performed after the light treatment or simultaneously performed with the light treatment, converts the silicon film into one having superior optical and electrical characteristics.

Examples of light sources used in the present invention include: low-pressure or high-pressure mercury lamps, deuterium lamps, discharge light of rare gases, such as argon, krypton, and xenon, YAG lasers, argon lasers, carbon dioxide lasers, excimer lasers of XeF, XeCl, XeBr, KrF, KrCl, ArF, and ArCl. These light sources



generally have power in a range of 10 to 5,000 W, and a power of 100 to 1,000 W is adequate in the present invention. The wavelengths of these light sources are not limited, as long as the light is absorbed in the coating film of the photo-ring-cleavage silicon compound to some extents, and are generally in a range of 170 nm to 600 nm.

5 The use of laser light is, particularly preferable, in view of conversion efficiency into the polycrystalline silicon film. The temperature for the light treatment is generally in a range of room temperature to 500°C, and can be appropriately determined depending on the semiconductive characteristics of the resulting silicon film.

The present invention will now be described in more detail with reference to  
10 the Examples, but should not be limited to these Examples.

In these Examples, the viscosity and the surface tension of each ink composition indicate values at 20°C.

#### (EXAMPLE 1)

A silicon-compound-containing solution (ink) is prepared by dissolving 0.05 g  
15 of cyclopentasilane into a mixed solvent of 7 g of decahydronaphthalene and 3 g of tetrahydronaphthalene. The viscosity of the solution is 3.2 mPa·s and the surface tension is 33 dyn/cm. Fig. 1 shows the patterning of silicon thin films by an ink jet process in accordance with this example. The silicon-compound-containing ink 11 is pattern-coated onto a quartz substrate 13 using an ink jet head 12 composed of a  
20 piezoelectric element in an argon atmosphere. The substrate is dried at 200°C, in an argon atmosphere, and is pyrolyzed, at 500°C, to form a pattern of metallic silicon films 15 (film regions, each having a diameter of 50 μm), each having a thickness of 35 nm, shown in Figs. 1(b) and 1(c). Fig. 1(b) is a cross-sectional view of the top view of Fig. 1(c). A surface analysis of the silicon film by ESCA detects only silicon  
25 atoms. The crystal state of the silicon film by a Raman spectrum is 100% amorphous. The amorphous silicon films are irradiated with an excimer laser having a wavelength of 308 nm and an energy density of 300 mJ/cm<sup>2</sup> in an argon atmosphere to form a pattern of polycrystalline silicon films 16 (film regions, each having a diameter of 50 μm) shown in Fig. 1(d). The Raman spectrum shows that the crystallinity is 80%.

## (EXAMPLE 2)

A silicon-compound-containing solution (ink) is prepared by dissolving 0.2 g of hexachlorocyclohexasilane into a mixed solvent of 5 g of cyclohexylbenzene and 5 g of cymene. The viscosity of the solution was 4.8 mPa·s and the surface tension is 32 dyn/cm. Fig. 2 shows the patterning of silicon thin films by an ink jet process in accordance with this example. The silicon-compound-containing ink 21 is pattern-coated onto a quartz substrate 23 using an ink jet head 22 composed of a piezoelectric element in an argon atmosphere. The substrate is dried at 250°C in an argon atmosphere containing 5% hydrogen and is heat-treated at 450°C while being irradiated with ultraviolet light from a 500-W high-pressure mercury lamp for 30 minutes to form a pattern of metallic silicon films 25 (film regions, each being 50 × 50 μm), each having a thickness of 80 nm, shown in Figs. 2(b) and 2(c). A surface analysis of the silicon film, by ESCA, detects only silicon atoms. The crystal state of the silicon film, by a Raman spectrum, is 100% amorphous. The amorphous silicon film was heat-treated at 800°C, in an argon/hydrogen atmosphere, to form a pattern of a polycrystalline silicon film 26 (film region of 50 × 50 μm) having a crystallinity of 50%, shown in Fig. 2(d).

## (EXAMPLE 3)

A silicon-compound-containing solution (ink) is prepared by dissolving 0.1 g of 1-borahexaprismane (Compound 11) into a mixed solvent of 7 g of tetrahydronaphthalene and 3 g of cyclohexylbenzene. The viscosity of the solution is 4.2 mPa·s and the surface tension is 36 dyn/cm. Fig. 3 shows the patterning of silicon thin films by an ink jet process in accordance with this example. The silicon-compound-containing ink 31 is pattern-coated onto a quartz substrate 33 using an ink jet head 32 composed of a piezoelectric element in an argon atmosphere. The substrate is dried at 250°C in an argon atmosphere and was pyrolyzed at 500°C to form a pattern of metallic silicon films 35 (film regions, each having a diameter of 50 μm), each having a thickness of 70 nm, shown in Figs. 3(b) and 3(c). A surface analysis of the silicon film, by ESCA, detects only silicon atoms and boron atoms and

the ratio thereof is 5:1. The crystal state of the silicon film, by a Raman spectrum, is 100% amorphous. The amorphous silicon films are irradiated with an excimer laser having a wavelength of 308 nm and an energy density of 350 mJ/cm<sup>2</sup> in an argon atmosphere to form a pattern of polycrystalline silicon films 36 (film regions, each having a diameter of 50 μm) shown in Fig. 3(d). The Raman spectrum shows that the crystallinity was 75%.

#### (EXAMPLE 4)

A silicon-compound-containing solution (ink) is prepared by dissolving 0.05 g of 1-phosphocyclopentasilane into a mixed solvent of 8 g of decahydronaphthalene and 2 g of cyclohexylbenzene. The viscosity of the solution is 4.0 mPa·s and the surface tension is 36 dyn/cm.

Fig. 4 shows the patterning of silicon thin films by an ink jet process in accordance with this example. The silicon-compound-containing ink 41 is pattern-coated onto a quartz substrate 43 using an ink jet head 42 composed of a piezoelectric element in an argon atmosphere. The substrate is dried at 150°C in an argon atmosphere containing 5% hydrogen while being irradiated with ultraviolet light from a 500-W high-pressure mercury lamp for 10 minutes to form a tough coating film of polysilazane which is insoluble in solvents by a ring cleavage reaction. The coating film is pyrolyzed at 500°C in an argon atmosphere to form a pattern of metallic silicon films 45 (film regions, each being 50 × 50 μm), each having a thickness of 25 nm, shown in Figs. 4(b) and 4(c). A surface analysis of the silicon film, by ESCA, detects only silicon atoms and phosphorus atoms and the ratio thereof is 5:1. The crystal state of the silicon film, by a Raman spectrum, is 100% amorphous. The amorphous silicon films are irradiated with an excimer laser having a wavelength of 308 nm and an energy density of 300 mJ/cm<sup>2</sup> in an argon atmosphere to form a pattern of polycrystalline silicon films 46 (film regions, each being 50 × 50 μm) shown in Fig. 4(d). The Raman spectrum shows that the crystallinity was 75%.

## (EXAMPLE 5)

A silicon-compound-containing solution (ink) is prepared by dissolving 0.5 g of silylcyclopentasilane into a mixed solvent of 5 g of decahydronaphthalene and 5 g of tetrahydronaphthalene. The viscosity of the solution is 5.2 mPa·s and the surface tension is 34 dyn/cm. Fig. 5 shows the patterning of silicon thin films by an ink jet process in accordance with this example. The silicon-compound-containing ink 51 is pattern-coated onto a polyimide film substrate 53 using an ink jet head 52 composed of a piezoelectric element in an argon atmosphere. The substrate is dried at 200°C in an argon atmosphere and is irradiated using a 500-W high-pressure mercury lamp at 350°C for photolysis and pyrolysis to form a pattern of metallic silicon films 55 (film regions, each having a diameter of 70  $\mu$ m), each having a thickness of 80 nm, shown in Fig. 5(b). A surface analysis of the silicon film by ESCA detects only silicon atoms. The crystal state of the silicon film, by a Raman spectrum, is 100% amorphous.

## (EXAMPLE 6)

A (p-type) silicon-compound-containing solution (ink) is prepared by dissolving 0.01 g of 1-boracyclopentasilane and 0.1 g of cyclopentasilane into a mixed solvent of 5 g of tetrahydronaphthalene and 5 g of cyclohexylbenzene. The viscosity of the solution is 3.8 mPa·s and the surface tension is 35 dyn/cm. Next, a (n-type) silicon-compound-containing solution (ink) is prepared by dissolving 0.01 g of 1-phosphocyclopentasilane and 0.1 g of cyclopentasilane into a mixed solvent of 5 g of tetrahydronaphthalene and 5 g of cyclohexylbenzene. The viscosity of the solution is 3.7 mPa·s and the surface tension is 36 dyn/cm. Fig. 6 shows the patterning of n-type and p-type silicon thin films by an ink jet process in accordance with this example. The (n-type) silicon-compound-containing ink 61 and the (p-type) silicon-compound-containing ink 64 are pattern-coated onto a quartz substrate 63 using an ink jet head 62 composed of a piezoelectric element in an argon atmosphere. The substrate is dried at 250°C, in an argon atmosphere containing 5% hydrogen, and is pyrolyzed at 500°C to form a pattern including n-type silicon films 25n (film regions, each being

50 × 50 μm) and p-type silicon films 25p (film regions, each being 50 × 50 μm) shown in Figs. 6(b) and 6(c). According to a surface analysis of the silicon films by ESCA, the ratio of silicon atoms and phosphorus atoms is 50:1 in the n type and the ratio of silicon atoms and phosphorus atoms is 50:1 in the p type. The crystal state of the silicon films, by a Raman spectrum, is 100% amorphous. The amorphous silicon films are irradiated with an excimer laser having a wavelength of 308 nm and an energy density of 320 mJ/cm<sup>2</sup> in an argon atmosphere to form a pattern of n-type and p-type polycrystalline silicon films 26n and 26p, respectively, (film regions, each being 50 × 50 μm) shown in Fig. 6(d). The Raman spectrum shows that the crystallinity is 75%.

#### (EXAMPLE 7)

A silicon-compound-containing solution (ink) is prepared by dissolving 0.05 g of octasilacubane (Compound 2) into a mixed solvent of 5 g of decahydronaphthalene and 5 g of tetrahydronaphthalene. The viscosity of the solution is 5.5 mPa·s and the surface tension is 34 dyn/cm. Fig. 7 shows the patterning of silicon thin films by an ink jet process in accordance with this example. The silicon-compound-containing ink 71 is pattern-coated onto a quartz substrate 73 using an ink jet head 72 composed of a piezoelectric element in an argon atmosphere containing 3% hydrogen. The substrate is irradiated with using a high-pressure mercury lamp of 500 W at room temperature for 5 minutes in an argon atmosphere containing 3% hydrogen. As a result, polyhydrosilane films, which are insoluble in solvents, were formed. The films are pyrolyzed in the argon atmosphere containing 3% hydrogen at 500°C to form a pattern of metallic silicon films 75 (film regions, each having a diameter of 50 μm), each having a thickness of 35 nm, shown in Figs. 7(b) and 7(c). Fig. 7(b) is a cross-sectional view and Fig. 7(c) is a top view corresponding to Fig. 7(b). A surface analysis of the silicon film, by ESCA, detects only silicon atoms. The crystal state of the silicon film, by a Raman spectrum, is 100% amorphous. The amorphous silicon films are irradiated with an excimer laser having a wavelength of 308 nm and an energy density of 300 mJ/cm<sup>2</sup> in an argon atmosphere to form a pattern of

polycrystalline silicon films 76 (film regions, each having a diameter of 50  $\mu\text{m}$ ) shown in Fig. 7(d). The Raman spectrum shows that the crystallinity is 80%. (Example 8)

5 The silicon-compound-containing solution of Example 7 is prepared and pattern-coated onto a quartz substrate using an ink jet head composed of a piezoelectric element in an argon atmosphere containing 3% hydrogen. The substrate is dried at 150°C in an argon atmosphere containing 3% hydrogen, and simultaneously is irradiated using a 500 W high-pressure mercury lamp for 5 minutes. As a result, polyhydrosilane films, which are insoluble in solvents, are formed. The films are pyrolyzed, as in Example 7, to form a pattern of amorphous metallic silicon films, as in Example 7. The amorphous silicon films are irradiated with an excimer laser having the wavelength and the same energy density as in Example 7, in air, to form a pattern of polycrystalline silicon films 76 (film regions, each having a diameter of 50  $\mu\text{m}$ ) shown in Fig. 7(d). The Raman spectrum shows that the crystallinity was 60%.

15 According to the present invention, as described above, a composition containing a silicon precursor is pattern-coated by an ink jet process, and a desired silicon film (pattern) as an electronic material, can be formed by a novel liquid phase process, which is different from conventional methods for forming silicon film, by means of thermal and/or optical energy.

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#### INDUSTRIAL APPLICABILITY

25 Since the present invention prevents the generation of powder during the formation of the silicon film and does not use a large vacuum process, unlike conventional CVD processes, the present invention does not require expensive equipment and can form a film on a substrate having a large area using minimum amounts of materials. Since the silicon film pattern can be formed without a photolithographic etching process, semiconductor devices having silicon films, such



## CLAIMS

(1) A method for forming a silicon film comprising applying by patterning an ink composition containing a silicon compound onto a substrate by an ink jet process.

5 (2) A method for forming a silicon film according to claim 1, wherein the ink composition is applied in an inert atmosphere.

(3) A method for forming a silicon film according to either claim 1 or 2, further comprising, after applying the ink composition containing the silicon compound onto the substrate by the ink jet process, a drying step of removing a solvent of the composition and a step of pyrolyzing an/or photolyzing in the coating film.

10 (4) A method for forming a silicon film according to claim 3, further comprising a step for irradiating the silicon film formed by the heat treatment and/or the light treatment with laser to convert the amorphous silicon film into a polycrystalline silicon film.

15 (5) A method for forming a silicon film according to claim 1, wherein the silicon compound is a silicon compound represented by the following general formula (I):



wherein n represents an integer 3 or more, m represents an integer of n, 2n-2, 2n, or 2n+2, and X represents a hydrogen atom and/or a halogen atom.

20 (6) A method for forming a silicon film according to claim 1, wherein the silicon compound is a silicon compound represented by the following general formula (II):



wherein X represents a hydrogen atom and/or a halogen atom, Y represents a boron atom or a phosphorus atom, a represents an integer of 3 or more, b represents an integer of a to 2a+c+2, and c represents an integer of 1 to a.

25 (7) A method for forming a silicon film according to claim 1, wherein the silicon compound is a composition containing a silicon compound represented by the following general formula (I) and a silicon compound represented by the following general formula (II):





wherein n represents an integer 3 or more, m represents an integer of n,  $2n-2$ ,  $2n$ , or  $2n+2$ , and X represents a hydrogen atom and/or a halogen atom;



5 wherein X represents a hydrogen atom and/or a halogen atom, Y represents a boron atom or a phosphorus atom, a represents an integer of 3 or more, b represents an integer of a to  $2a+c+2$ , and c represents an integer of 1 to a.

(8) A method for forming a silicon film according to either claim 5 or 7, wherein n is in a range of 5 to 20 in the general formula (I).

10 (9) A method for forming a silicon film according to either claim 6 or 7, wherein a+c  
is in a range of 5 to 20 in the general formula (II).

(10) A method for forming a silicon film according to any one of claims 1 to 9, wherein, in the composition, the silicon compound is dissolved in at least one solvent having a vapor pressure at room temperature of 0.001 to 50 mmHg.

15       (11) A method for forming a silicon film according to claim 10, wherein the solvent is a hydrocarbon solvent.

(12) A method for forming a silicon film according to any one of claims 1 to 11, wherein the concentration of the silicon compound in the composition is in a range of 0.01 to 10 percent by weight.

20 (13) A method for forming a silicon film according to any one of claims 1 to 12,  
wherein the concentration has a viscosity of 1 to 50 mPa·s and a surface tension of 20  
to 70 dyn/cm.

(14) An ink-jet ink composition for forming a silicon film, comprising a silicon compound represented by the general formula (I):



wherein n represents an integer 3 or more, m represents an integer of n,  $2n-2$ ,  $2n$ , or  $2n+2$ , and X represents a hydrogen atom and/or a halogen atom.

(15) An ink-jet ink composition for forming a silicon film, comprising a silicon compound represented by the general formula (II):



wherein X represents a hydrogen atom and/or a halogen atom, Y represents a boron atom or a phosphorus atom, a represents an integer of 3 or more, b represents an integer of a to  $2a+c+2$ , and c represents an integer of 1 to a.

- 5 (16) An ink-jet ink composition for forming a silicon film, comprising a silicon compound represented by the following general formula (I) and a silicon compound represented by the following general formula (II):



wherein n represents an integer 3 or more, m represents an integer of n,  $2n-2$ ,  $2n$ , or  $2n+2$ , and X represents a hydrogen atom and/or a halogen atom;



wherein X represents a hydrogen atom and/or a halogen atom, Y represents a boron atom or a phosphorus atom, a represents an integer of 3 or more, b represents an integer of a to  $2a+c+2$ , and c represents an integer of 1 to a.

- 15 (17) An ink composition according to either claim 14 or 16, wherein n is in a range of  
5 to 20 in the general formula (I).

- (18) An ink composition according to either claim 15 or 16, wherein  $a+c$  is in a range of 5 to 20 in the general formula (II).

- (19) An ink composition according to any one of claims 14 to 18, wherein the silicon  
20 compound is dissolved in at least one solvent having a vapor pressure at room  
temperature of 0.001 to 50 mmHg.

- (20) An ink composition according to claim 19, wherein the solvent is a hydrocarbon solvent.

- (21) An ink composition according to any one of claims 14 to 20, wherein the  
25 concentration of the silicon compound in the composition is in a range of 0.01 to 10  
percent by weight.

- (22) An ink composition according to any one of claims 14 to 21, wherein the concentration has a viscosity of 1 to 50 mPa·s and a surface tension of 20 to 70 dyn/cm.

An ink composition 1 containing a silicon precursor is selectively discharged into predetermined regions on a substrate from an ink jet head 2 to form a pattern of the silicon precursor, and is subjected to a heat and/or light treatment to convert the silicon precursor into an amorphous silicon film 5 or a polycrystalline silicon film 6. A silicon film pattern is thereby obtained on a large area at low cost with low energy.

5

09/701534  
526 Rec'd PCT/PTO 30 NOV 2000

**PATENT APPLICATION**

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of

Shunichi SEKI, Tatsuya SHIMODA,  
Satoru MIYASHITA, Masahiro FURUSAWA,  
Ichio YUDASAKA, Yasuo MATSUKI,  
Yasumasa TAKEUCHI

Application No.: U.S. National Stage of PCT/JP00/01987

Filed: November 30, 2000

Docket No.: 107291

For: METHOD FOR FORMING SILICON FILM AND INK COMPOSITION FOR INK JET

**REQUEST FOR APPROVAL OF DRAWING CORRECTIONS**

Director of the U.S. Patent and Trademark Office  
Washington, D.C. 20231

Sir:

The Examiner is requested to review and approve the 7 substitute drawing sheets,  
marked in red on the attached copy of such drawing figures.

Upon approval by the Examiner, and upon allowance of this application, the formal  
drawings will be corrected.

Respectfully submitted,

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Registration No. 46,527

JAO:CAH/cmm

Date: November 30, 2000

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09/701534-13000

1/7

FIG. 1

Fig. 1(a)

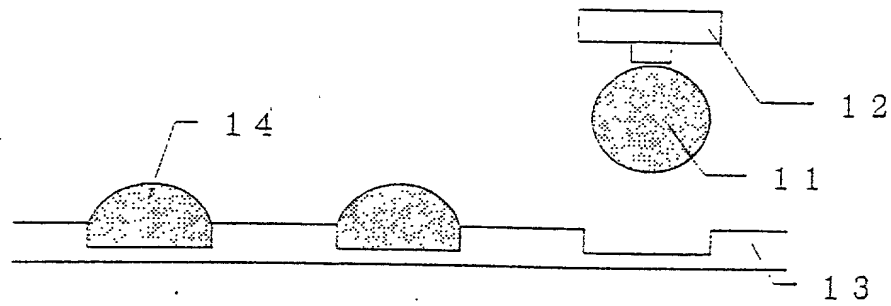


Fig. 1(b)

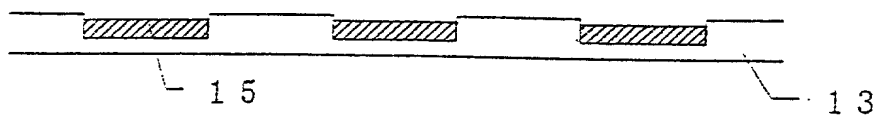


Fig. 1(c)

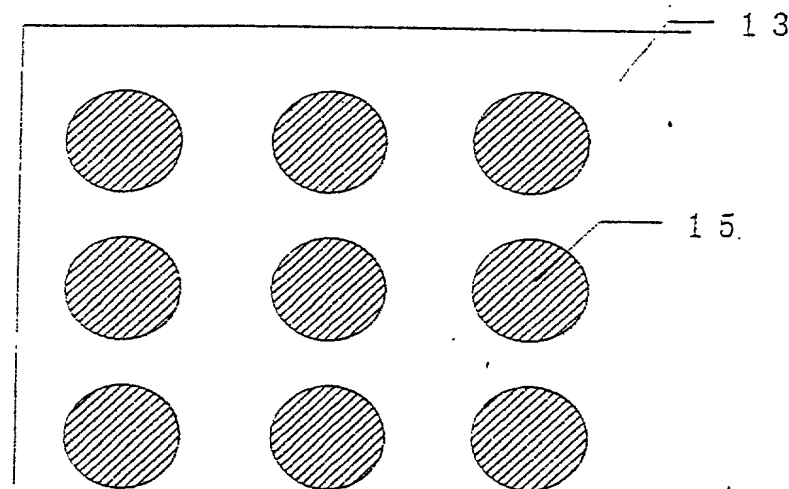
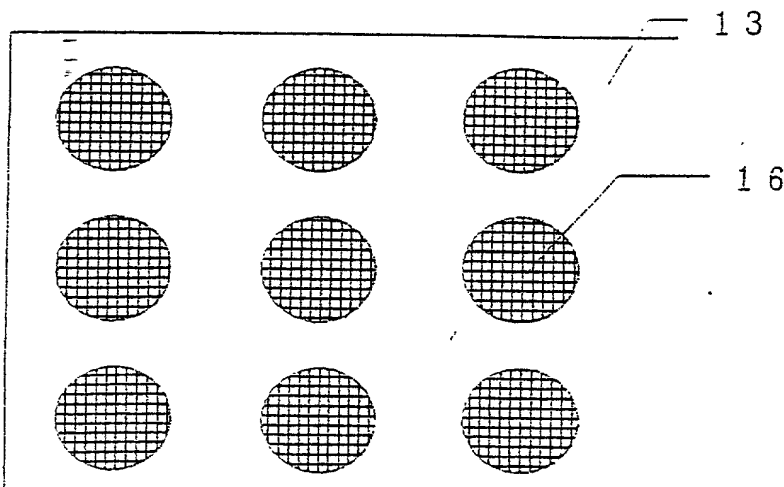


Fig. 1(d)



~~FIG. 2~~

Fig. 2 (a)

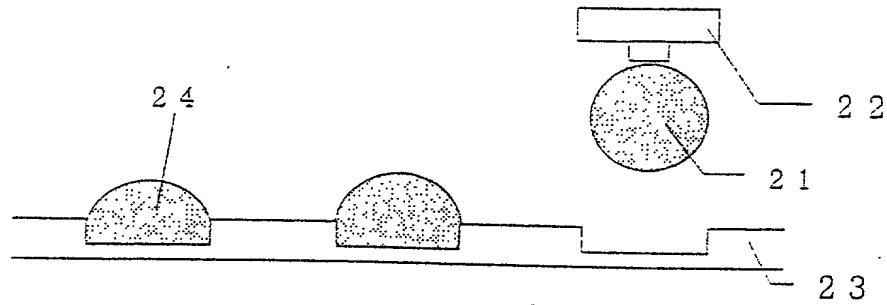


Fig. 2 (b)

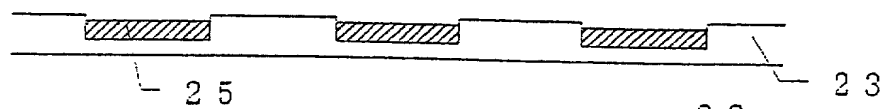


Fig. 2(c)

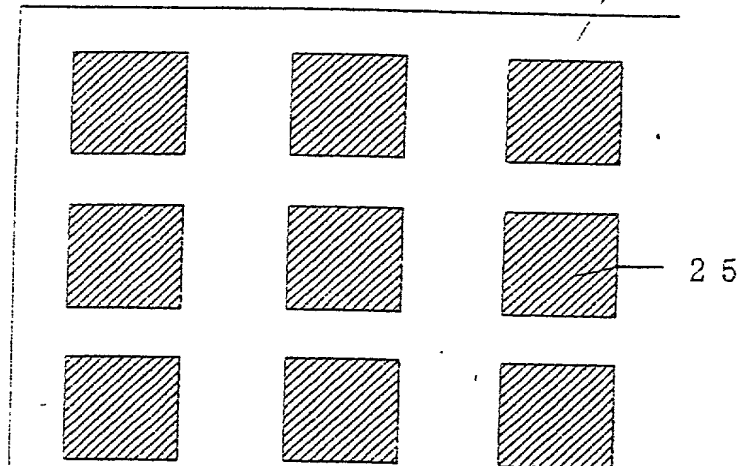


Fig. 2 (d)

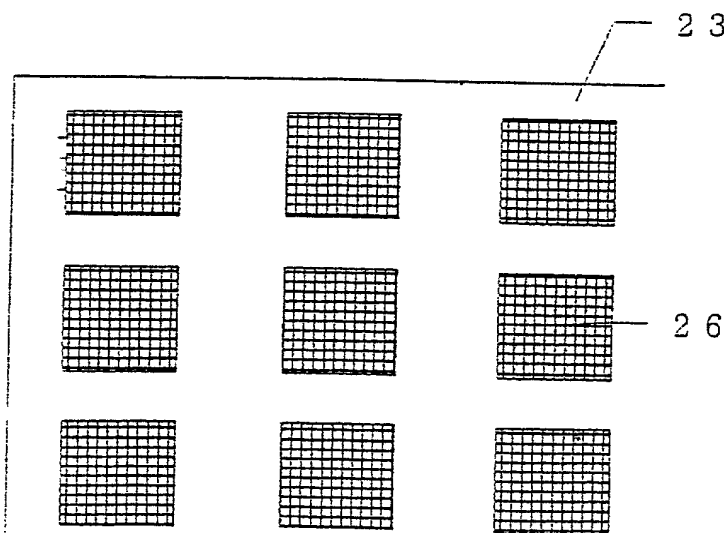


Fig. 3 (a)

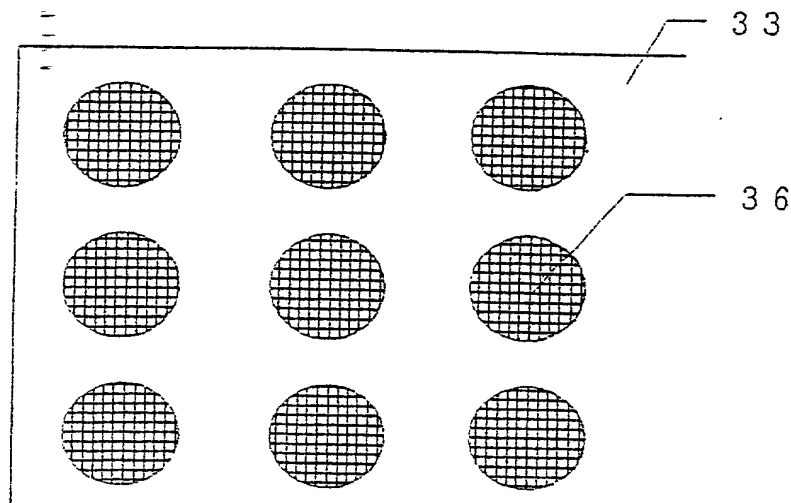
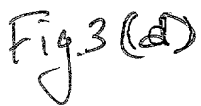
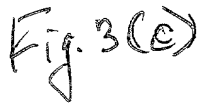
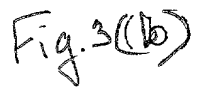






Fig. 5 (a)

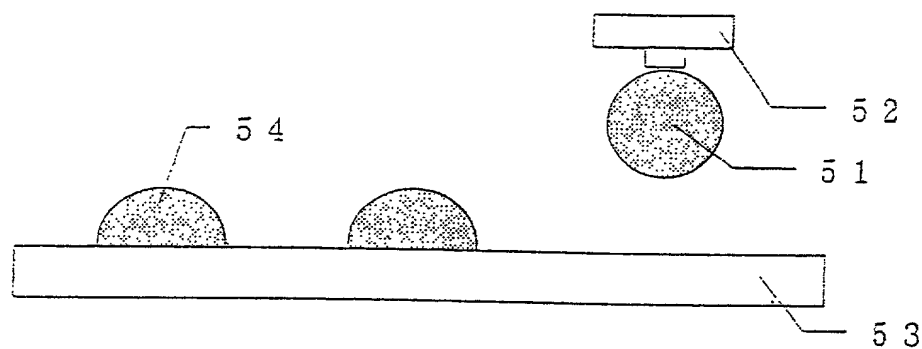
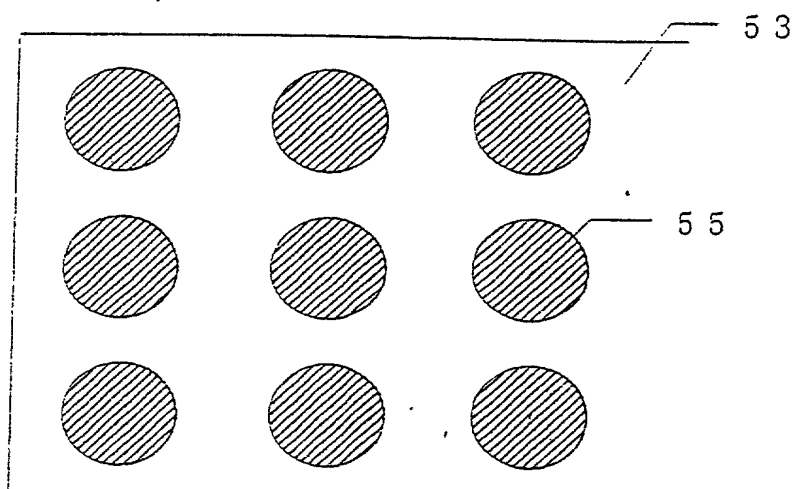


Fig. 5 (b)



6/7

FIG. 6

Fig. 6 (a)

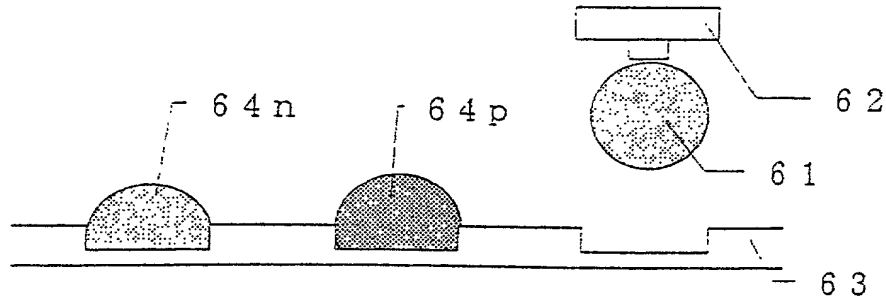


Fig. 6 (b)

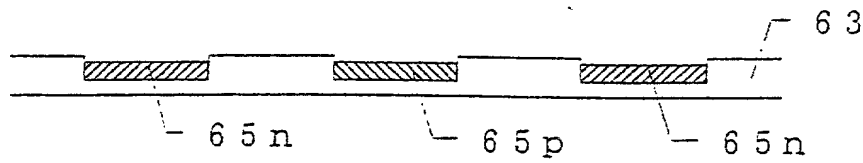


Fig. 6 (c)

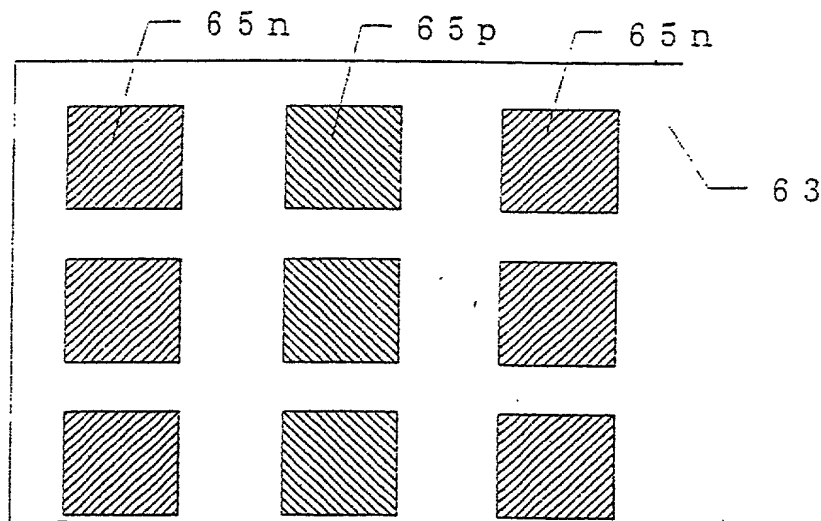
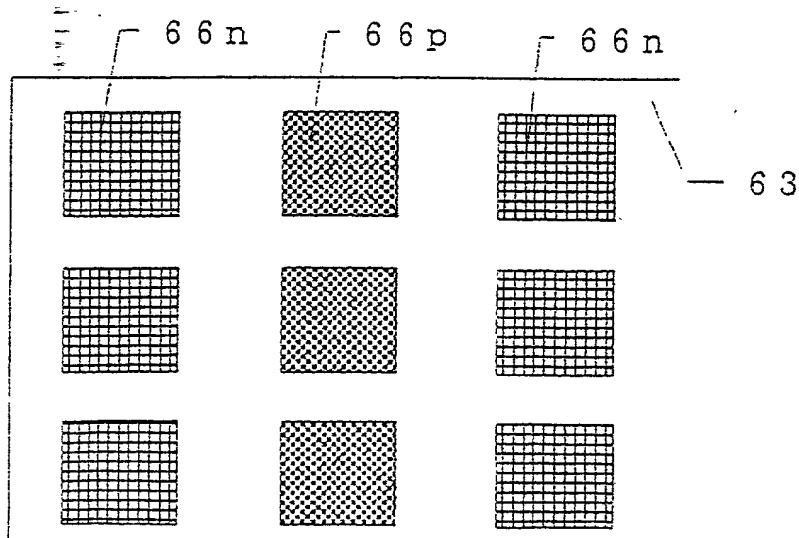


Fig. 6 (d)



7/7

FIG. 7

Fig. 7 (a)

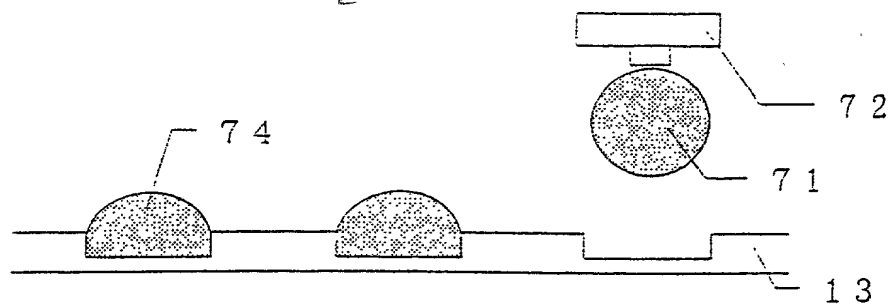


Fig. 7 (b)

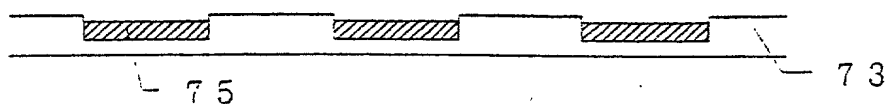


Fig. 7 (c)

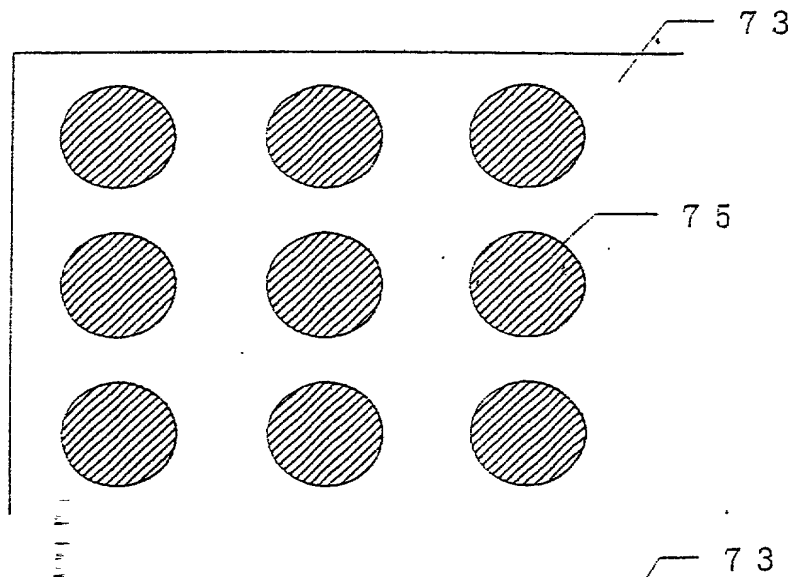
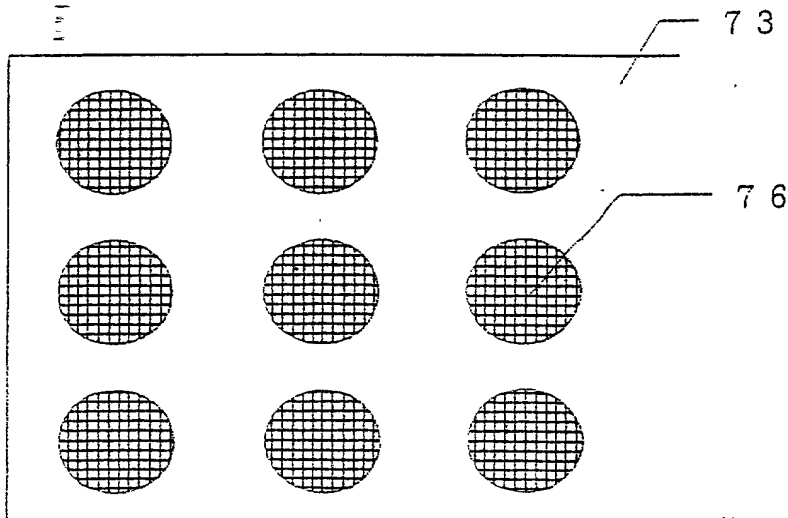
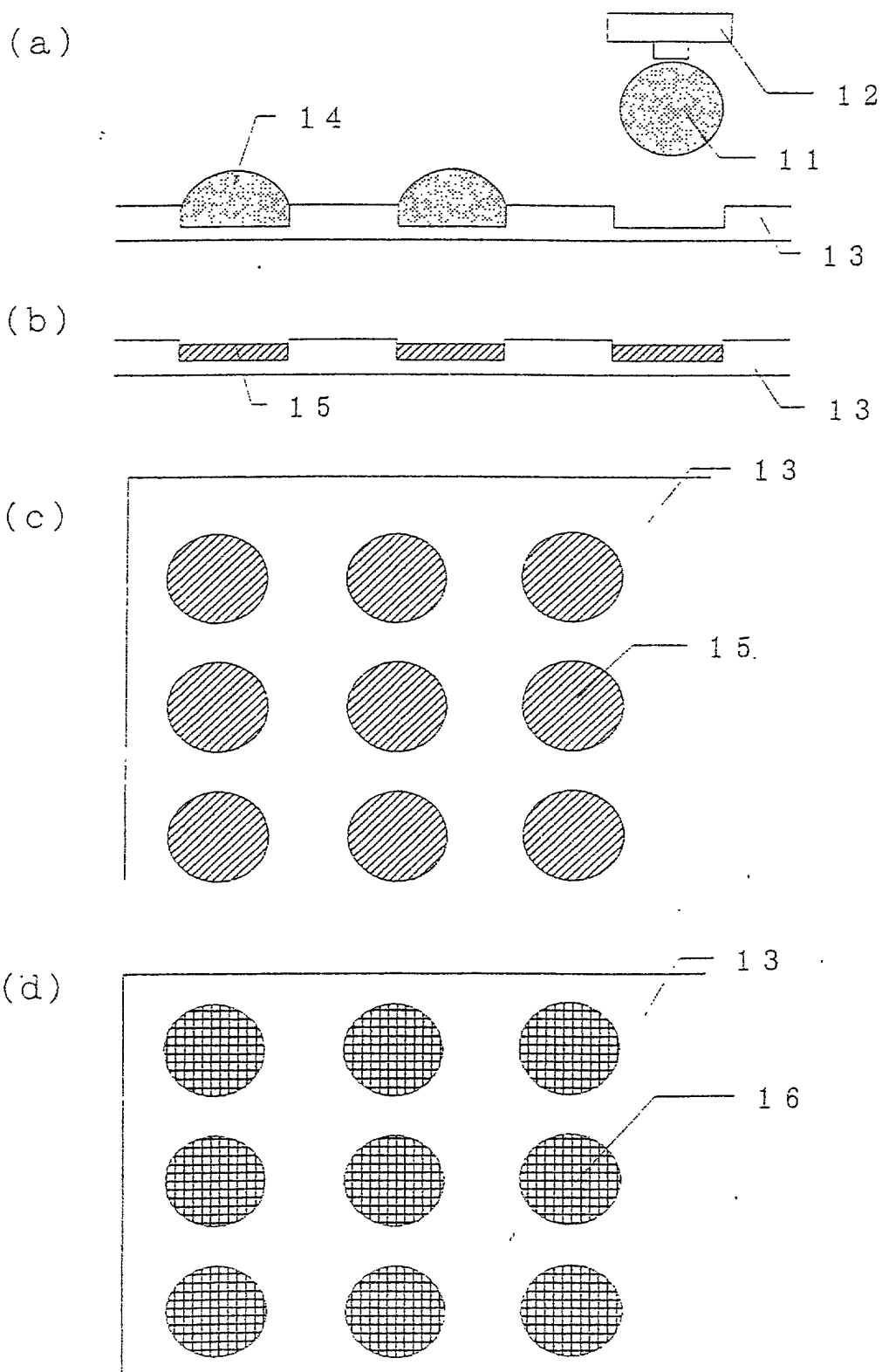


Fig. 7 (d)



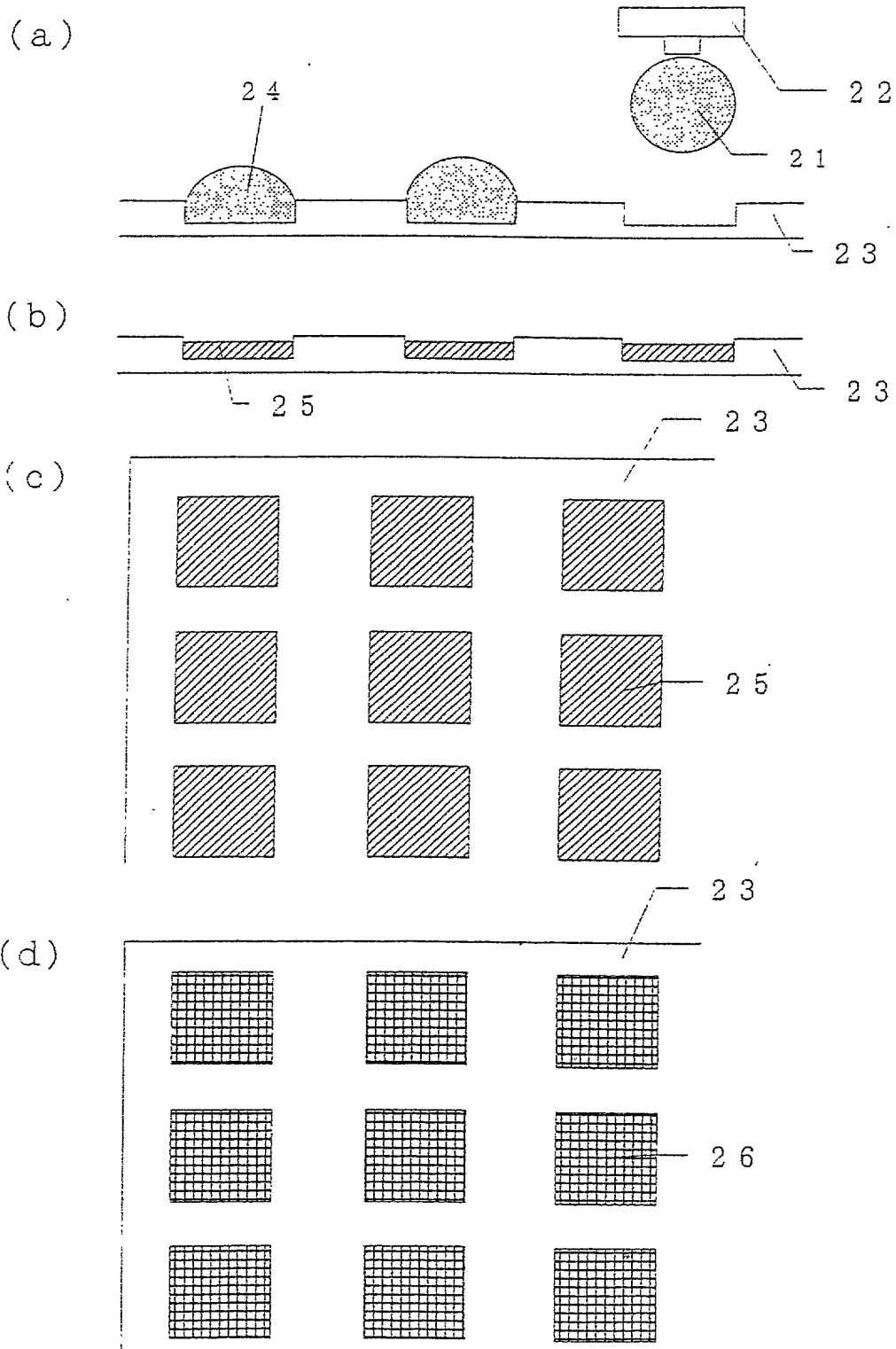
1/7

FIG. 1



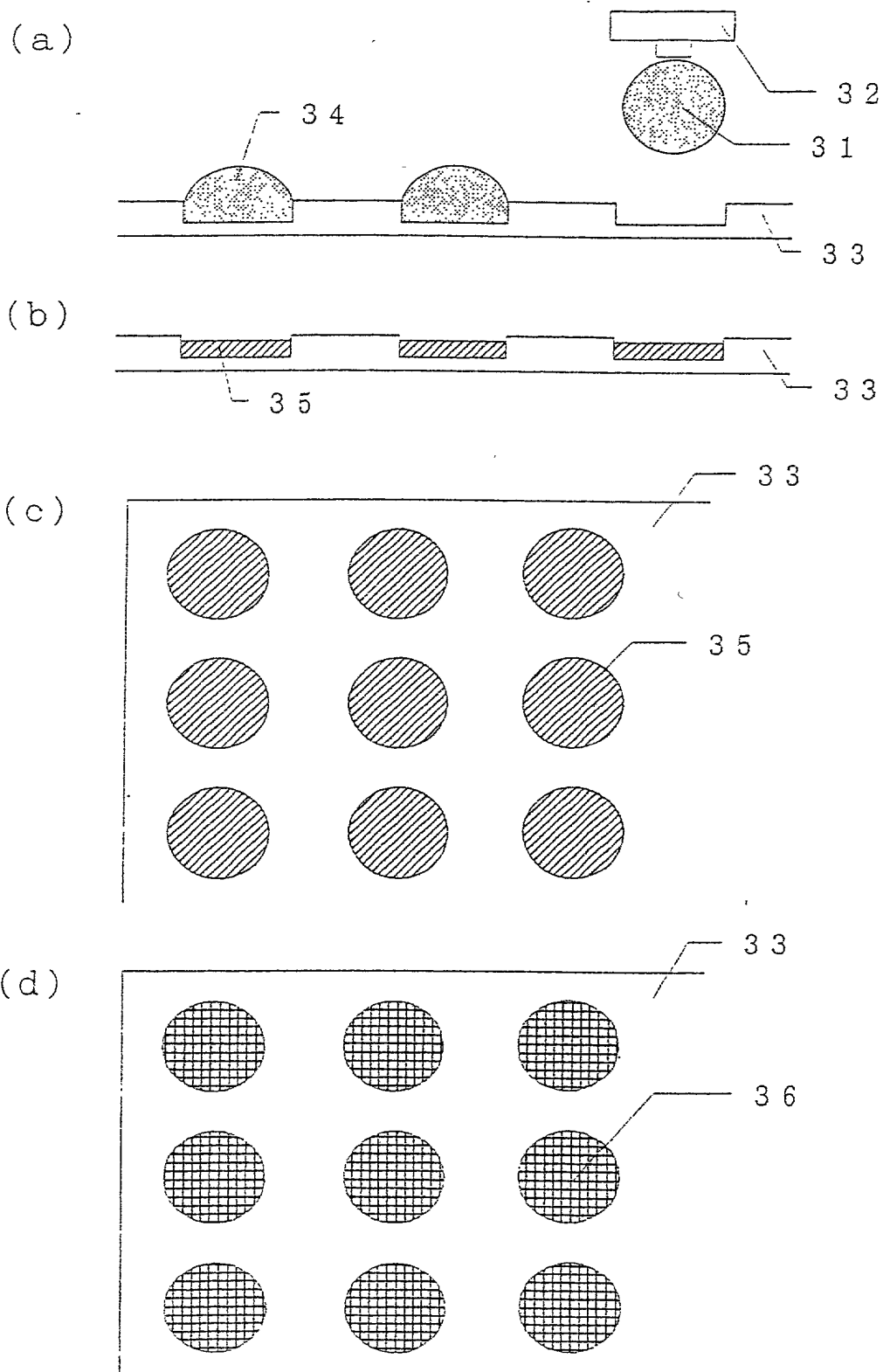
2/7

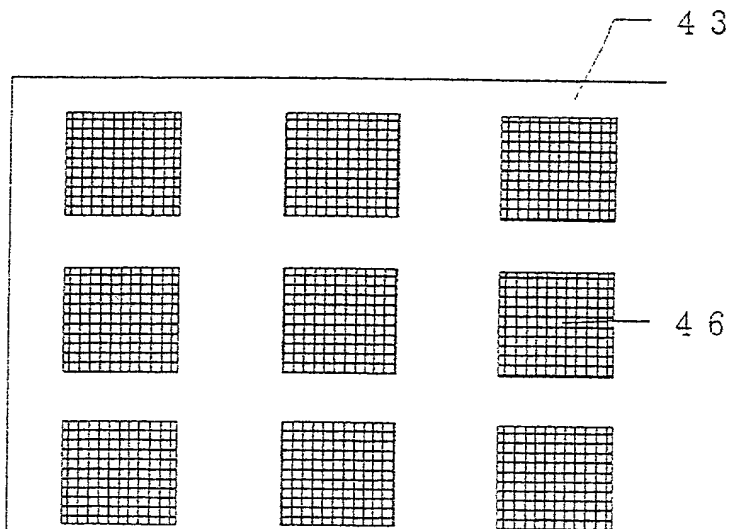
FIG. 2



3/7

FIG. 3

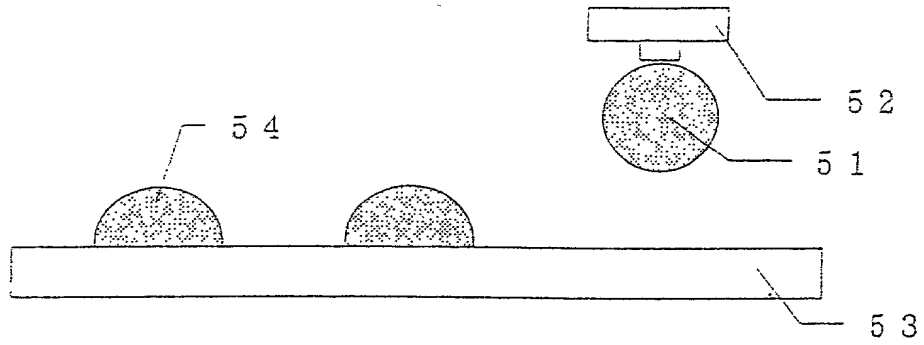




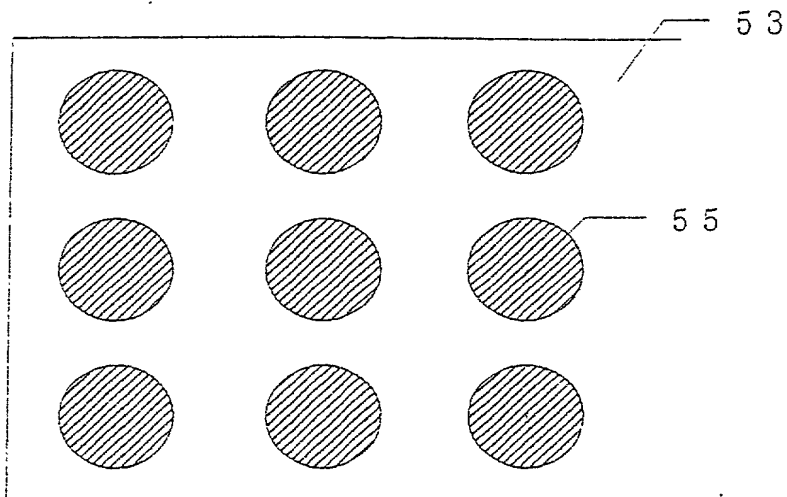
5/7

FIG. 5

(a)



(b)









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**Seiko Epson Ref. No.: F005063US00**

Attorney's Ref. No.: 107291

## Declaration and Power of Attorney For Patent Application

特許出願宣言書及び委任状

## Japanese Language Declaration

日本語宣言書

下記の氏名の発明者として、私は以下の通り宣言します。

As a below named inventor, I hereby declare that:

私の住所、私書箱、国籍は、下記の私の氏名の後に記載された通りです。

My residence, post office address and citizenship are as stated next to my name.

下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者（下記の氏名が一つの場合）もしくは最初かつ共同発明者であると（下記の名称が複数の場合）信じています。

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

## シリコン膜形成方法およびインクジェット用インク組成物

## METHOD FOR FORMING SILICON FILM AND INK COMPOSITION FOR INK JET

上記発明の明細書（下記の欄で×印がついていない場合は、本書に添付）は、

the specification of which is attached hereto unless the following box is checked:

☐ \_\_\_\_\_に提出され、米国出願番号または  
特許協定条約 国際出願番号を \_\_\_\_\_ とし、  
(該当する場合) \_\_\_\_\_ に訂正されました。

☐ was filed on \_\_\_\_\_  
as United States Application Number or  
PCT International Application Number  
\_\_\_\_\_ and was amended on  
\_\_\_\_\_ (if applicable).

私は、特許請求範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

私は、連邦規則法典第 3 7 編第 1 条 5 6 項に定義されるとおり、特許資格の有無について重要な情報を開示する義務があることを認めます。

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

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I hereby claim foreign priority under Title 35, United States Code, Section 119 (a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

**Prior Foreign Application(s)**

外国での先行出願

**Priority Not Claimed**

優先権主張なし

11-090311(P)Japan30/March/ 1999

(Number)

(Country)

(Day/Month/Year Filed)

(番号)

(国名)

(出願年月日)



(Number)

(Country)

(Day/Month/Year Filed)

(番号)

(国名)

(出願年月日)



私は、第35編米国法典119条(e)項に基づいて下記の米国特許出願規定に記載された権利をここに主張いたします。

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(Application No.)(Filing Date)(Application No.)(Filing Date)

(出願番号)

(出願日)

(出願番号)

(出願日)

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PCT/JP00/0198729/March/2000Pending

(Application No.)

(Filing Date)

(Status: Patented, Pending, Abandoned)

(出願番号)

(出願日)

(現況: 特許許可済、係属中、放棄済)

(Application No.)

(Filing Date)

(Status: Patented, Pending, Abandoned)

(出願番号)

(出願日)

(現況: 特許許可済、係属中、放棄済)

私は、私自身の知識に基づいて本宣言書中で私が行なう表明が真実であり、かつ私が入手した情報と私の信じることに基づく表明が全て真実であると信じていること、さらに故意になされた虚偽の表明及びそれと同等の行為は米国法典第18編第1001条に基づき、罰金または拘禁、もしくはその両方により処罰されること、そしてそのような故意による虚偽の声明を行なえば、出願した、又は既に許可された特許の有効性が失われることを認識し、よってここに上記のごとく宣誓を致します。

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Date \_\_\_\_\_

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**Japanese Language Declaration**

(日本語宣言書)

委任状： 私は、下記の発明者として、本出願に関する一切の手続きを米特許商標局に対して遂行する弁理士または代理人として、下記の者を指名いたします。(弁護士、または代理人の氏名及び登録番号を明記のこと)

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Edward P. Walker, (Reg. 31,450)  
Robert A. Miller, (Reg. 32,771)  
Mario A. Costantino, (Reg. 33,565)  
Caroline D. Dennison, (Reg. 34,494)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (list name and registration number)

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第七共同発明者の署名

日付

Seventh inventor's signature

Date

Yasumasa Takeuchi 27/10/00

住所

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日付

Eighth inventor's signature

Date

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Residence

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国籍

Citizenship

私書箱

Post Office Address

(第九以降の共同発明者についても同様に記載し、署名をすること)

(Supply similar information and signature for ninth and subsequent joint inventors.)